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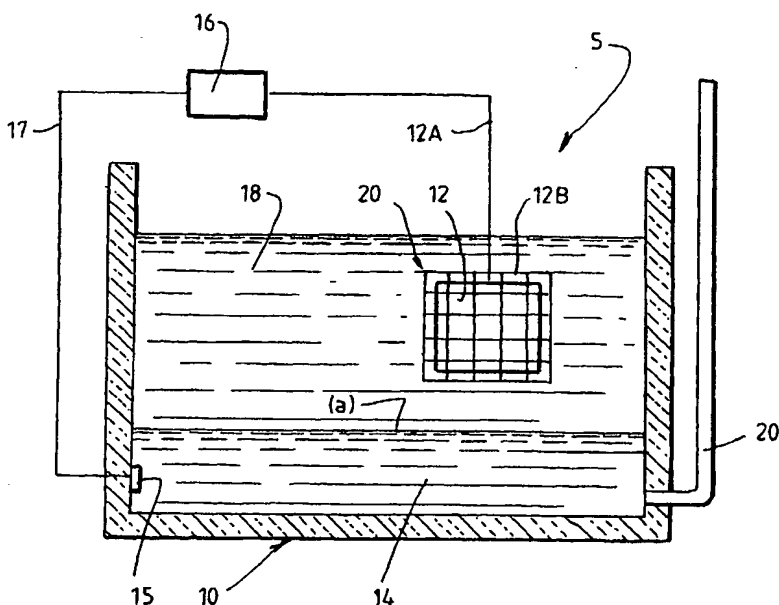
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ELECTROLYTIC REDUCTION OF METAL OXIDES



(57) Abstract: An electrolytic cell and a method of electrolytically reducing a metal oxide (such as titania) in a solid state are disclosed. The electrolytic cell includes (a) a molten electrolyte, (b) a cathode in contact with the electrolyte, the cathode being formed at least in part from the metal oxide, and (c) a molten metal anode (such as silver or copper) in contact with the electrolyte.

## ELECTROLYTIC REDUCTION OF METAL OXIDES

## 1. Field of the Invention

5           The present invention relates to electrolytic reduction of metal oxides.

## 2. Background of and Prior Art to the Invention

10           The present invention was made during the course of an on-going research project on the electrolytic reduction of titania ( $\text{TiO}_2$ ) carried out by the applicant.

15           During the course of the research project the applicant carried out experimental work on an electrolytic cell that included a graphite crucible that formed an anode of the cell, a pool of molten  $\text{CaCl}_2$ -based electrolyte in the crucible, and a cathode that included solid titania.

20           The  $\text{CaCl}_2$ -based electrolyte was a commercially available source of  $\text{CaCl}_2$ , namely calcium chloride dihydrate, that decomposed on heating and produced a very small amount of  $\text{CaO}$ .

25           The applicant operated the electrolytic cell at a potential above the decomposition potential of  $\text{CaO}$  and below the decomposition potential of  $\text{CaCl}_2$ .

30           The applicant found that the cell could electrolytically reduce titania to titanium with very low concentrations of oxygen.

35           The applicant does not have a clear understanding of the electrolytic cell mechanism at this stage. Nevertheless, whilst not wishing to be bound by the comments in this paragraph, the applicant offers the

- 2 -

following comments by way of an outline of a possible cell mechanism. The applicant believes that operating the experimental electrolytic cell above a potential at which the  $\text{CaCl}_2$ -based electrolyte partially decomposed had the result of producing  $\text{Ca}^{++}$  cations that migrated to the vicinity of the titania in the cathode and provided a driving force that facilitated extraction of  $\text{O}^{--}$  anions produced by electrolytic reduction of titania to titanium in the cathode. The applicant also believes that the  $\text{O}^{--}$  anions, once extracted from the titania, migrated to the anode and reacted with anode carbon and produced CO and released electrons that facilitated electrolytic reduction of titania to titanium in the cathode. In addition, the applicant believes that carbon in the anode reacted with  $\text{Ca}^{++}$  cations and produced a complex calcium carbide. The experimental work carried out by the applicant produced evidence of Ca metal in the electrolyte. The applicant believes that the Ca metal was the result of electrodeposition of  $\text{Ca}^{++}$  cations as Ca metal on electrically conductive sections of the cathode and that at least part of the Ca metal dissolved in the electrolyte and migrated to the vicinity of the titania in the cathode and participated in chemical reduction of oxides.

However, notwithstanding that the cell could electrolytically reduce titania to titanium with very low concentrations of oxygen, the applicant also found that there were relatively significant amounts of carbon transferred from the anode to the electrolyte and to the titanium produced at the cathode under a wide range of cell operating conditions. Carbon in the titanium is an undesirable contaminant. In addition, carbon transfer was responsible for low energy efficiency of the cell. Both problems are significant barriers to commercialisation of electrolytic reduction technology.

The applicant carried out experimental work to

- 3 -

identify the mechanism for carbon transfer and to determine how to minimise carbon transfer and/or to minimise the adverse effects of carbon transfer.

5     3.             Summary of Invention

Broadly, the invention resides in replacing the carbon anode with a molten metal anode.

10             According to the present invention there is provided an electrolytic cell for electrolytic reduction of a metal oxide in a solid state, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode formed at least in part from the metal oxide in contact with the  
15     electrolyte, and (c) a molten metal anode in contact with the electrolyte.

              Preferably the metal of the molten metal anode has a relatively high saturation level for oxygen at the  
20     operating temperature of the cell.

              Preferably the metal is chosen such that its melting point is within the operating temperature ranges of the electrolyte.

25             Preferably the melting point of the metal of the molten metal anode is higher than the melting point of the electrolyte and lower than the vaporisation and/or decomposition temperature of the electrolyte in order to  
30     prevent electrolyte consumption and removal through vaporisation.

              Preferably the metal of the molten metal anode has a very low solubility in the molten electrolyte at the  
35     cell operating temperatures, as high solubility is detrimental because the anode metal will deplete and deposit on the cathode. The latter might not be a serious

- 4 -

problem where there is low solubility and reactivity of the metal with the cathode metal at the operating temperature.

5                    Preferably the metal of the molten metal anode is silver or copper.

10                   The solubility of oxygen in the Ag-O system at 1000°C is around 0.32% by weight. Ag has a melting point of 960°C, which is about 300 to 100°C above the melting point of alkali and alkaline earth halides that provide suitable electrolytes.

15                   The solubility of oxygen in the Cu-O system at 1100°C is 0.39% by weight. The melting point of copper is 1083°C, which is well below the boiling points of the above mentioned electrolytes.

20                   Preferably the electrolytic cell further includes a means for removing oxygen that has diffused into the molten metal anode from the cell.

25                   Such an "oxygen scavenging pump" means can have a number of different forms.

30                   One option includes a duct that communicates with the molten metal anode and a device to create a partial pressure reduction between the molten metal anode and a head of molten metal within the duct.

35                   An advantage of an "oxygen scavenging pump" means is that the amount of the molten metal anode required can be minimised, since the saturation wt% limits of oxygen within the molten anode metal are no longer the sole determining parameter of oxygen uptake by the anode.

For example, in order to reduce 10g of titania to

- 5 -

pure titanium, 1 kg Ag would be required in the absence of an oxygen scavenging pump means to remove substantially all of the oxygen from the molten metal anode. Continuous removal of oxygen from the molten metal anode facilitated by the means allows the process to be performed continuously, as compared with batch processing.

According to the present invention there is also provided a method of electrolytically reducing a metal oxide in a solid state in an electrolytic cell, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode in contact with the electrolyte, the cathode being formed at least in part from the metal oxide, and (c) a molten metal anode in contact with the electrolyte, which method includes applying a cell potential across the anode and the cathode.

Preferably the method includes maintaining the cell temperature above the melting points of the electrolyte and the metal of the metal anode.

Preferably the method includes maintaining the cell temperature below the vaporisation and/or decomposition temperatures of the electrolyte.

Preferably the method includes applying a cell potential above a decomposition potential of at least one constituent of the electrolyte so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

Preferably the metal oxide is a titanium oxide.

It is preferred that the metal oxide be titania.

In a situation in which the metal oxide is titania it is preferred that the electrolyte be a  $\text{CaCl}_2$ -

- 6 -

based electrolyte that includes CaO as one of the constituents.

5 In such a situation it is preferred that the method includes maintaining the cell potential above the decomposition potential for CaO.

10 It is also preferred that the method includes maintaining the cell potential below the decomposition potential for  $\text{CaCl}_2$ .

It is preferred that the method includes maintaining the cell potential less than 3.0V.

15 It is preferred particularly that the method includes maintaining the cell potential below 2.5V.

20 It is preferred more particularly that the method includes maintaining the cell potential below 2.0V.

It is preferred that the method includes maintaining the cell potential at least 1.5V.

25 The following example illustrates an application of the invention in the process of reducing titania into substantially pure titanium using an electrolytic cell constructed in accordance with the present invention and as illustrated schematically in Figure 1.

#### 30 4. Description of Exemplary Embodiment

Figure 1 is a schematic illustration of a electrolytic cell that can be scaled-up in application of the present invention.

35

Whilst the example described below relates to the electrolytic reduction of titania, the basic principle is

- 7 -

equally applicable to other metal oxides, in particular oxides of Si, Ge or alloys containing these metals.

5 With reference to the figure, the electrolytic cell 5 includes a graphite-free crucible 10 made of a suitable refractory material that is essentially inert as regards reaction with the electrolyte and electrode materials described below at cell operating temperatures of between 1000°C and 1200°C.

10

The electrolytic cell further includes a pool 18 of molten  $\text{CaCl}_2$  electrolyte within the crucible 10.

15 The electrolytic cell 5 further includes a pool 14 of molten silver or copper (within the crucible 10). The molten Ag or Cu forms the anode 14 of the cell. In view of the different densities, the molten metal anode 14 is below the molten electrolyte pool 18.

20

The electrolytic cell 5 further includes a titania plate 12 positioned within a cage 12b. The cage 12b (and therefore the plate 12) is suspended into the crucible 10 by means of a lead 12a. This assembly forms the cathode 20 of the cell.

25

30 The electrolytic cell 5 further includes a power source 16 and electrical connections between the power source 16 and the anode 14 and the cathode 20. The connections include electrical leads 17 and 12a and a suitable high-temperature resistant plate member 15, preferably of stainless steel, that provides electric connection between the interior of crucible 10 (and thus anode 14) and the lead 17.

35

In use, power source 16 provides for constant potential (voltage) settings thereby allowing the cell 5 to draw the amount of charge required during the



- 8 -

electrolytic refining of the metal oxide body at a selectable potential.

5 The electrolytic cell 5 further includes type B thermocouples contained in heat-resistant, inert sheaths (not illustrated) for monitoring temperature in the molten metal anode 14 and the molten electrolyte 18.

10 The electrolytic cell 5 further includes a refractory tube 20 that connects the interior of the crucible 10, below the molten metal anode bath level (a), with a device for imparting a negative pressure differential between anode bath 14 and the head (b) of molten Ag suctioned into the tube 20. The pressure  
15 differential need only be slight to provide a driving force for diffusion and transport of oxygen that is dissolved into the metal anode bath 14 into the tube 20 which is preferably vented to atmosphere.

20 In use, the above-described electrolytic cell 5 is positioned in a suitable furnace to maintain the electrolyte and the anode metal in their respective molten states. The atmosphere around the crucible 10 is preferred to be an inert gas, such as argon, that does not  
25 react with the molten electrolyte.

Once the cell reaches its operating temperature, about 1150 to 1200°C, depending on the anode metal employed, a constant voltage of around 2.5-3 V is applied  
30 between the cell electrodes 12 and 14, the cell potential being above the decomposition potential of CaO in the electrolyte but below the decomposition potential of  $\text{CaCl}_2$ , whereby reduction of the titania in the cathode is carried out as described above.

35

The oxygen that passes into the electrolyte 18 is subsequently transported to the metal bath anode 14 where

- 9 -

it dissolves. The dissolved oxygen then diffuses through the molten anode bath 14 under the pressure differential imparted through duct 20 and is released as O<sub>2</sub> into the surrounding atmosphere.

5

As will be noted, this transport mechanism is effective for as long as oxygen in the molten metal anode is below the saturation level.

10

By way of example, it is noted that other shapes and configurations of the titania cathode 20 are equally employable, bearing in mind the need to ensure proper electric contact between the power source 16 and the titania to be reduced within the cell.

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- 10 -

## CLAIMS:

1. An electrolytic cell for electrolytic reduction of a metal oxide in a solid state, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode in contact with the electrolyte, the cathode being formed at least in part from the metal oxide, and (c) a molten metal anode in contact with the electrolyte.
2. The electrolytic cell defined in claim 1 wherein the metal of the molten metal anode has a relatively high saturation level for oxygen at the operating temperature of the cell.
3. The electrolytic cell defined in claim 1 or claim 2 wherein the metal of the molten metal anode is chosen such that its melting point is within the operating temperature ranges of the electrolyte.
4. The electrolytic cell defined in any one of the preceding claims wherein the melting point of the metal of the molten metal anode is higher than the melting point of the electrolyte and lower than the vaporisation and/or decomposition temperature of the electrolyte.
5. The electrolytic cell defined in any one of the preceding claims wherein the metal of the molten metal anode has a very low solubility in the molten electrolyte at the cell operating temperatures,
6. The electrolytic cell defined in any one of the preceding claims wherein the metal of the molten metal anode is silver or copper.
7. The electrolytic cell defined in any one of the preceding claims further includes a means for removing oxygen that has diffused into the molten metal anode from

- 11 -

the cell.

8. The electrolytic cell defined in claim 7 wherein the cell oxygen removal means includes a duct that  
5 communicates with the molten metal anode and a device to create a partial pressure reduction between the molten metal anode and a head of molten metal within the duct.

9. A method of electrolytically reducing a metal  
10 oxide in a solid state in an electrolytic cell, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode in contact with the electrolyte, the cathode being formed at least in part from the metal oxide, and (c) a molten metal anode in contact with the electrolyte, which  
15 method includes applying a cell potential across the anode and the cathode.

10. The method defined in claim 9 includes  
maintaining the cell temperature above the melting points  
20 of the electrolyte and the metal of the metal anode.

11. The method defined in claim 9 or claim 10  
includes applying a cell potential above a decomposition  
potential of at least one constituent of the electrolyte  
25 so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

12. The method defined in any one of claims 9 to 11  
wherein the metal oxide is a titanium oxide.  
30

13. The method defined in any one of claims 9 to 11  
wherein the metal oxide is titania.

14. The method defined in any one of claims 9 to 13  
35 wherein the electrolyte is a  $\text{CaCl}_2$ -based electrolyte that includes  $\text{CaO}$  as one of the constituents.

- 12 -

15. The method defined in claim 14 includes maintaining the cell potential above the decomposition potential for CaO.

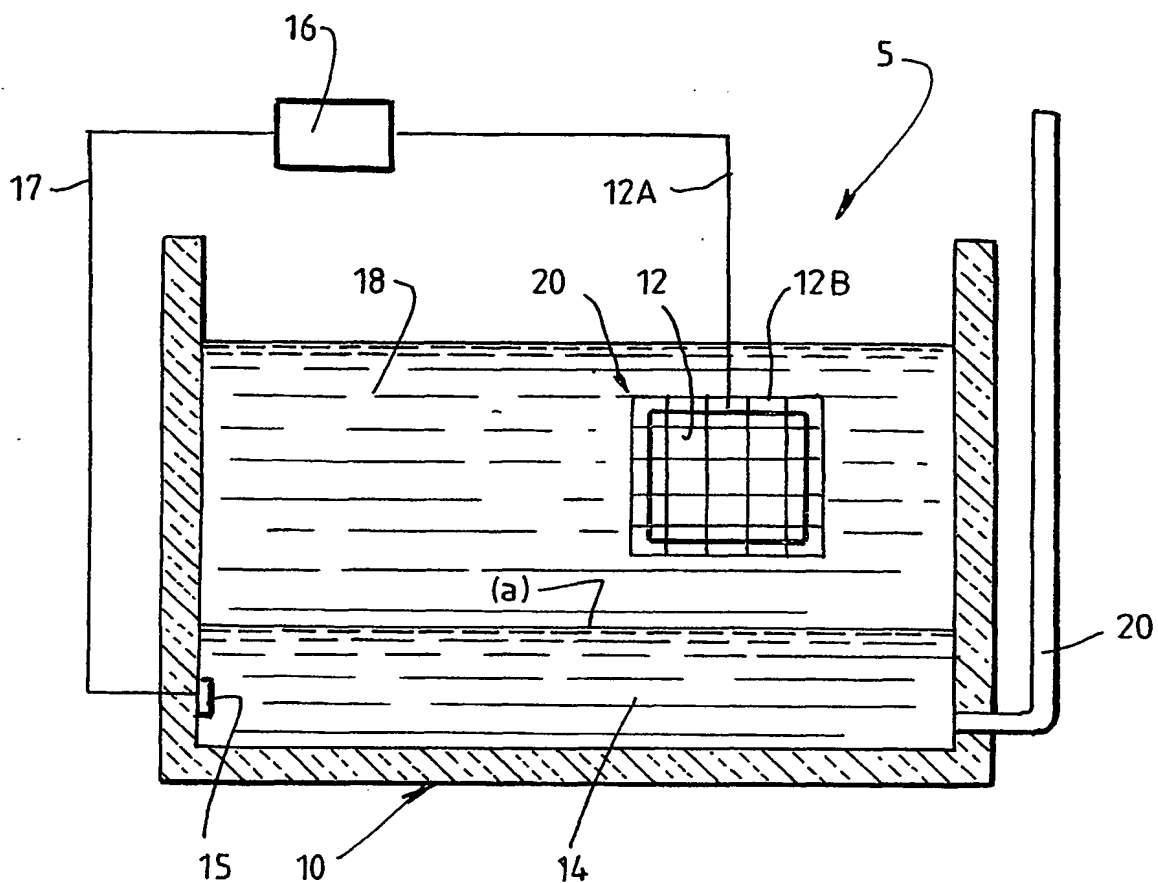
5 16. The method defined in claim 14 or claim 15 includes maintaining the cell potential below the decomposition potential for  $\text{CaCl}_2$ .

10 17. The method defined in claim 14 or claim 15 includes maintaining the cell potential below 3.0V.

18. The method defined in claim 14 or claim 15 includes maintaining the cell potential below 2.5V.

15 19. The method defined in claim 14 or claim 15 includes maintaining the cell potential below 2.0V.

20. The method defined in any one of claims 14 to 20 includes maintaining the cell potential at least 1.5V.



III.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/00457

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int. Cl. <sup>7</sup> : C25C 3/18, 3/28		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC: C25C 3/18, 3/28		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
DWPI		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2359564 A (THE SECRETARY OF STATE FOR DEFENCE UK) 29 August 2001 whole document	1-20
A	WO 98/33956 A (CATHINGOTS LIMITED) 6 August 1998 whole document	1-20
A	WO 99/64638 A (CAMBRIDGE UNIVERSITY TECHNICAL SERVICES LIMITED) 16 December 1999 whole document	1-20
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 14 June 2002		Date of mailing of the international search report 19 JUN 2002
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  B. PREMARATNE Telephone No : (02) 6283 2407

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU02/00457

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5006209 A (BECK et al.) 9 April 1991 whole document	1-20
A	US 4875985 A (DONAHUE et al.) 24 October 1989 whole document	1-20



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/AU02/00457**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
GB	2359564	AU	200133871	AU	200133876	AU	200133890
		WO	200162994	WO	200162995	WO	200162996
		GB	2362164				
WO	9833956	AU	81918/98	BR	9807156	EP	958409
		IT	TO		970080	NO	993455
		NZ	337553	US	6074545	ZA	9800897
WO	9964638	AU	42770/99	BR	9910939	CZ	20004476
		EP	1088113	HU	200102934	NO	20006154
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US	5006209	AU	72598/91	BR	9106039	CA	2075892
		NO	923150	WO	9112357		
US	4875985	CA	1337020	EP	440711	WO	9004043
		US	4964973				
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